

UDC 666.113.621'33'27'18'.001.8

SYNTHESIS AND PROPERTIES OF SODIUM-BOROPHOSPHATE AND SODIUM-ALUMOPHOSPHATE GLASSES

T. K. Pavlushkina¹ and O. A. Gladushko¹

Translated from *Steklo i Keramika*, No. 6, pp. 16 – 18, June, 2000.

The effect of additives of boron orthophosphate on the properties of metaphosphate glasses is considered for vitreous sodium and aluminum metaphosphates. It is established that BPO_4 has a positive effect on the resistance of the glasses to hydrofluoric acid and water.

We have studied the structure and properties of binary metaphosphate glasses in [1]. We established that the introduced cations can be classified into two groups in accordance with their effect on the properties of the glasses. The first group comprises metaphosphates of alkaline, alkaline-earth, and triple-charged cations, in which all the parameters reflecting the strength of the lattice (the temperatures of glass transition t_g and softening t_f , the TCLE, the frequency of vibrations of the phosphorus – oxygen bonds $\nu_{\text{P-O}}$) change steadily with growth in the force of the field and the polarization capacity of the cation, which indicates that the structure of the glass strengthens. The resistance of the glass to hydrofluoric acid and water increases simultaneously.

The second group comprises glasses bearing double-charged cations of elements of auxiliary subgroups, i.e., Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} . In this group with cations having an easily deformable 18-charged electron shell the growth in the force of the field of the cation is also accompanied by a strengthening action on the $[\text{PO}_4]$ tetrahedron, which is reflected by the increase in t_g , t_f and $\nu_{\text{P-O}}$ and a decrease in the TCLE. Due to the high deformability of the cations they are affected considerably by the counterpolarizing action of the oxygen of the lattice, which causes the formation of flexible, chemically strong covalent M-O bonds. The action of oxygen is the stronger the greater the polarizability and lower the force of the field of the cation; therefore, the resistance of glasses of the second group to hydrofluoric acid increases with decrease in the force of the field of the cation.

Thus, the chemical resistance to hydrofluoric acid increases in the following succession: alkaline metaphosphates – alkaline-earth metaphosphates – metaphosphates of Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and trivalent elements. The water resistance increases from alkaline metaphosphates through Cu^{2+} , Zn^{2+} ,

Cd^{2+} , Pb^{2+} metaphosphates and alkaline-earth metaphosphates to metaphosphates of trivalent elements.

The discovered rules allowed us to assume that the resistance to hydrofluoric acid and water should be considerably increased by the introduction of boron orthophosphate into the glasses. The cation of boron metaphosphate is characterized by a high force of the field, a high polarizing power, and the susceptibility to formation of B-O-P bridge bonds: this has been confirmed for glasses of the $x\text{BPO}_4 - (100-x)\text{LiPO}_3$ system where x was changed from 0 to 25% (here and below in mole fractions, if not specifically indicated).

In the present work we continued to study the effect of additives of boron orthophosphate on the properties of metaphosphate glasses. We synthesized a $25\text{BPO}_4 - 75\text{NaPO}_3$ composition and determined its properties. Comparing the properties of sodium-phosphate glass without BPO_4 and with 25% boron orthophosphate we established that it has a positive effect on the chemical stability of the glass. The loss in the mass after a 1-h treatment by hydrofluoric acid decreased from 388 to 1.5 mg/cm². The loss in the mass of sodium borophosphate glass after 5-h boiling in water amounted to 1.4 mg/cm², whereas the sodium-phosphate glasses did not resist even atmospheric moisture. The growth in the chemical resistance was accompanied by a growth in the characteristic temperatures (t_g increased from 245 to 378°C and t_f increased from 269 to 400°C) and a decrease in the TCLE from 178×10^{-7} to $110 \times 10^{-7} \text{ K}^{-1}$.

It should be noted that lithium- and sodium-phosphate glasses bearing $\geq 15\%$ BPO_4 possess a high crystallizability. Upon secondary treatment, crystals appear at 530 – 600°C. The optimum amount of BPO_4 additive is 10%, which provides low-melting but chemically stable noncrystallizable glasses.

¹ Institute of Glass Joint-Stock Company, Moscow, Russia.

TABLE 1

Grade of glass	Mole fraction, %, of			Temperature, °C		TCLE, 10^{-7} K^{-1}	Loss in the mass, mg/cm^2	
	P_2O_5	Al_2O_3	B_2O_3	glass transition	softening		upon 1-h treatment in hydrofluoric acid	upon 5-h treatment in boiling water
19	67.5	32.5	—	722	762	54	0.35	0
501	66.5	26.5	7.5	683	718	48	0.32	0.09
105	66.2	22.4	11.5	660	712	49	0.06	0.02
109	65.3	33.4	1.3	734	774	57	0.44	0.04
304	63.5	21.1	15.4	668	706	54	0.35	0
1103	63.2	24.3	12.5	704	736	57	0.36	0
206	62.6	25.9	11.5	754	724	57	0.53	0.06
17	61.3	38.7	—	750	825	61	2.40	0
602	61.2	26.6	12.2	670	706	41	3.24	0.023
103	57.3	20.8	21.9	738	768	57	3.50	0
510	13.6	13.4	73.0	671	703	48	67.00	0
710	10.8	30.7	58.5	675	706	71	75.10	0.03
610	10.7	27.7	61.6	698	727	28	38.00	0.17
711	10.0	45.0	45.0	684	716	40	31.50	0.03

The properties of glasses in the $\text{Al}(\text{PO}_3)_3 - \text{BPO}_4$ system present interest because BPO_4 is structurally similar to AlPO_4 and at the same time is lower-melting. It is known that vitreous BPO_4 with a stoichiometric composition cannot be obtained in an open system. We have synthesized glasses in the $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{P}_2\text{O}_5$ system. The synthesis was performed in a crucible furnace with gas heating in corundum crucibles with a capacity of 0.5 liter. The initial materials were monoammonium phosphate, aluminum oxide, and boric acid. The charge was enriched with an excess amount of P_2O_5 (12%) and B_2O_3 (7 wt.%) with allowance for the loss to volatilization. The glass was melted at a temperature of 1500–1600°C with a hold of 50–80 min at the maximum temperature.

It was established that the system possesses two regions of transparent glass, i.e., a high-phosphate one with 53–69% P_2O_5 , 10–40% Al_2O_3 , and 1–30% B_2O_3 , and a low-phosphate one with 10–13% P_2O_5 , 20–45% Al_2O_3 , and 35–70% B_2O_3 , which agrees with the data of [2, 3]. The high-phosphate range of transparent glass lies below the pseudobinary line of $\text{Al}(\text{PO}_3)_3 - \text{BPO}_4$ and its upper boundary passes in parallel to this line. Between the regions of transparent glass lie compositions that either sinter or crystallize with the formation of $\text{B}(\text{OH})_3$, $2\text{B}_2\text{O}_3 \cdot 9\text{Al}_2\text{O}_3$, and $\text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ solid solutions. In the low-phosphate range we established, in addition to the transparent glasses, opalescent glasses with compositions bearing an elevated amount of B_2O_3 (up to 70%). Electron micrographs show that they have a segregation structure.

Glasses obtained in this system possess physicochemical properties varying in a quite wide range. The temperatures of glass transition and softening for them are 670–740 and 706–774°C, respectively, the TCLE varied from 26×10^{-7} to $71 \times 10^{-7} \text{ K}^{-1}$ in the range 20–300°C, the density varies

from 2.15 to 2.53 g/cm^3 , and the refractive index varies from 1.500 to 1.535. The glasses are highly transparent in the range 0.3–3.0 μm and do not exhibit selective absorption. The loss in mass after 1-h treatment with hydrofluoric acid and after 5-h boiling in water fluctuates between 31.50 and 0.06 mg/cm^2 (hydrofluoric acid) and from 17 mg/cm^2 to 0 (water). Table 1 presents the thermal properties and the chemical stability of the glasses. The compositions have been determined by chemical analysis.

When analyzing the dilatometric properties of glasses of the studied system we noticed in some cases an "anomalous" dependence of the characteristic temperatures and the TCLE, namely, t_g and t_f changed in a symbatic manner with respect to the TCLE.

Glasses of the high-phosphate region had a high resistance to hydrofluoric acid. This group includes such compositions as, for example, $22.4\text{Al}_2\text{O}_3 - 11.5\text{B}_2\text{O}_3 - 66.2\text{P}_2\text{O}_5$. The loss in the mass of this glass due to 1-h treatment with hydrofluoric acid is 0.06 mg/cm^2 , which is an order of magnitude lower than in aluminum metaphosphate. The loss in mass of a glass with a less stable composition ($20.8\text{Al}_2\text{O}_3 - 21.9\text{B}_2\text{O}_3 - 57.3\text{P}_2\text{O}_5$) in hydrofluoric acid is equal to 3.5 mg/cm^2 . Glasses from the low-phosphate range, which contain 10–13% P_2O_5 , are much less acid-resistant; here the loss in mass is 31.5–75.0 mg/cm^2 .

When boiled in water for 5 h, high-phosphate glasses lose from 0 to 0.09 mg/cm^2 mass, and low-phosphate glasses lose 0.03–0.17 mg/cm^2 .

A study of the structure of alumoborophosphate glasses with the help of x-ray and vibration spectroscopy has shown that the structure of the glass of the high-phosphate region is represented by a combination of polyphosphate chains and tetrahedron elements. With growth in the proportion of P_2O_5 the motif of polyphosphate chains bonded by $\text{P}-\text{O}-\text{B}_{\text{IV}}$ and $\text{P}-\text{O}-\text{Al}_{\text{IV}}$ bridges becomes predominant. The deficit of phosphorus causes the formation of a skeleton structure of $[\text{AlO}_4]$, $[\text{BO}_4]$, and $[\text{PO}_4]$ tetrahedra. As the content of P_2O_5 decreases from 65 to 50%, the energy shift of the Alk_α lines in the x-ray spectra of the glasses changes from 0.75×10^{-19} to $0.32 \times 10^{-19} \text{ J}$ (from 0.47 to 0.20 eV), which corresponds to the transformation of aluminum from six-coordination into four-coordination. In crystalline $\text{Al}(\text{PO}_3)_3$ (the coordination number of aluminum is 6) and AlPO_4 (the coordination number of aluminum is 4) the shifts range from 0.82×10^{-19} to $0.29 \times 10^{-19} \text{ J}$ (0.51 and 0.18 eV), respectively.

In glasses from the low-phosphate region the elements of the structure of aluminum orthophosphate are combined with a boron-oxygen anion from polymerized BO_3 triangles.

It is obvious that the high acid resistance of glasses in the high-phosphate region is caused by the higher degree of polymerization of the phosphorus-oxygen tetrahedra.

Since the results of the structural analysis have shown that the net of high-phosphate glasses is represented by structural fragments of $\text{Al}(\text{PO}_3)_3$, AlPO_4 , and BPO_4 , it is expedient to express the compositions of the studied glasses in terms of fractions of these compounds in order to determine the effect of boron orthophosphate on the chemical stability and analyze the change in the decrease in mass after treatment by hydrofluoric acid and water as a function of the content of BPO_4 .

The properties of some alumoborophosphate glasses are presented in Table 2.

It can be seen that the substitution of aluminum orthophosphate by boron orthophosphate has a positive effect on the resistance to hydrofluoric acid and decreases the refractoriness of the glass. When a composition containing 55% AlPO_4 and 45% $\text{Al}(\text{PO}_3)_3$ is enriched with 34% BPO_4 instead of AlPO_4 the losses in mass upon treatment in hydrofluoric acid decrease from 2.40 to 0.06 mg/cm^2 , and t_f decreases from 825 to 712°C. In glasses bearing about 35% $\text{Al}(\text{PO}_3)_3$ the growth in the content of BPO_4 from 30 to 42% due to AlPO_4 reduces the loss in mass in hydrofluoric acid from 0.53 to 0.35 mg/cm^2 and t_f from 774 to 706°C. The loss in mass upon boiling in water is insignificant and there is no tendency for a change in the water resistance.

The decrease in the softening temperature with growth in the amount of BPO_4 in glass due to AlPO_4 is accompanied by a decrease in the TCLE, which seems to be caused by the lower thermal strength of the $\text{B}_{\text{IV}}-\text{O}$ bond ($372.91 \times 10^6 \text{ J/kg atom}$ or 89 kcal/g atom) as compared with $\text{Al}_{\text{IV}}-\text{O}$ ($423.19 \times 10^6 \text{ J/kg atom}$ or 101 kcal/g atom) at a substantially smaller size of the $[\text{BO}_4]$ tetrahedron (1.53 Å) as compared with the $[\text{AlO}_4]$ tetrahedron (1.72 Å).

The simultaneous growth in the t_f and in the TCLE can be explained by the fact that the growth in the content of AlPO_4 increases the proportion of short chains, increases the number of bonding bridges, and causes the formation of a denser structure. Since the internal mobility of the short chains in this case decreases, i.e., their rigidity increases, the structure becomes denser, which causes an increase in the TCLE too.

The phenomena of symbatic variation of the characteristic temperatures and the TCLE have been determined earlier in a study of binary vitreous metaphosphates [4] for the case where the composition deviated from the metaphosphate one towards diminished contents of P_2O_5 .

Studies of the properties of alkaline- and alumophosphate glasses with additives of boron orthophosphate have shown its positive effect on their chemical stability. The introduction of BPO_4 into alkaline metaphosphate glasses

TABLE 2

Grade of glass	Mole fraction, %			Temperature of softening, °C	TCLE, 10^{-7} K^{-1}	Loss in the mass, mg/cm^2	
	AlPO_4	BPO_4	$\text{Al}(\text{PO}_3)_3$			upon 1-h treatment in hydrofluoric acid	upon 5-h treatment in boiling water
19	46.0	—	54.0	762	54	0.35	0
17	55.0	—	45.0	825	61	2.40	0
109	52.0	4.0	44.0	774	57	0.44	0.04
501	28.7	22.3	49.0	718	48	0.32	0.09
105	18.4	34.0	47.6	712	49	0.06	0.02
206	35.6	30.7	33.7	774	58	0.53	0.06
1003	30.0	34.0	36.0	736	57	0.36	0
304	21.0	42.0	37.0	706	54	0.35	0

causes the formation of cross links between the chains, increases the degree of polymerization of the skeleton of the glass, and strengthens the phosphorus-oxygen bonds due to the action of a strong B^{3+} cation. The strengthening of the structure is accompanied by elevation of the chemical resistance to hydrofluoric acid and water.

The structure of vitreous metaphosphate characterized by "nonstoichiometry" bears $[\text{AlO}_4]$ tetrahedra, which connect the chains, in addition to the polyphosphate chains containing $[\text{AlO}_6]$ octahedra. Due to the high spatial connectedness of the net and the high strength of the $\text{P}-\text{O}$ bonds caused by the force of the Al^{3+} cation, this glass possesses a high chemical stability. The substitution of the $[\text{AlO}_4]$ tetrahedra by $[\text{BPO}_4]$ increases the resistance of the glass to hydrofluoric acid due to the higher strength of the $\text{B}_{\text{IV}}-\text{O}$ bonds as compared with the $\text{Al}_{\text{IV}}-\text{O}$ bonds.

Indeed, since boron oxide possesses more manifested acid properties than aluminum oxide and alkaline oxides, the replacement of $\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$, $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ or $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ by $\text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ in the composition of the glass increases its acidity.

The effect of BPO_4 on the thermal properties of alkaline- and alumophosphate glasses is ambiguous. Since the introduction of BPO_4 into an alkaline metaphosphate glass causes a transformation from a chain structure to a spatial one and strengthening of the $\text{P}-\text{O}$ bonds, this increases the characteristic temperatures and decreases the TCLE.

In an alumophosphate glass the introduction of BPO_4 causes replacement of the AlO_4 bonding elements by BPO_4 ones and does not on the whole change the degree of connectedness of the net. Due to the lower thermal strength and the shorter length of the $\text{B}_{\text{IV}}-\text{O}$ bonds as compared to the $\text{Al}_{\text{IV}}-\text{O}$ bonds, the introduction of BPO_4 causes a decrease in the temperatures of glass transition and softening and in the TCLE of the glass.

The use of the results of the present study will make it possible to design compositions of multicomponent phosphate glasses proceeding from the specified combination of their service properties.

REFERENCES

1. T. K. Pavlushkina and O. Gladushko, "Chemical stability of binary metaphosphate glasses," *Fiz. Khim. Stekla*, **13**(4), 606 - 611 (1987).
2. T. S. Zhukova, G. I. Artamonova, and Z. M. Syritskaya, "Glass formation and some properties of glasses in the $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{P}_2\text{O}_5$ system," *Tr. Inst. GIS*, No. 2, 3 - 6 (1977).
3. R. M. Klein and A. G. Kolbeck, "Glass formation and properties in the aluminum borophosphate system," *Am. Ceram. Soc. Bull.*, **57**(2), 199 - 202 (1978).
4. M. I. Kuz'menkov, V. V. Pechkovskii, and S. V. Plyshevskii, "A dilatometric study of vitreous metaphosphates of alkaline-earth metals," *Izv. Akad. Nauk SSSR. Ser. Neorg. Mater.*, **10**(3), 509 - 512 (1974).